FCC Gasoline Treating Using Catalytic Distillation

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Dr. Mitchell E. Loescher

Gasoline of the Future

- Lead is out
- Olefins reduced
- Aromatics reduced
- Benzene reduced
- Sulfur reduced

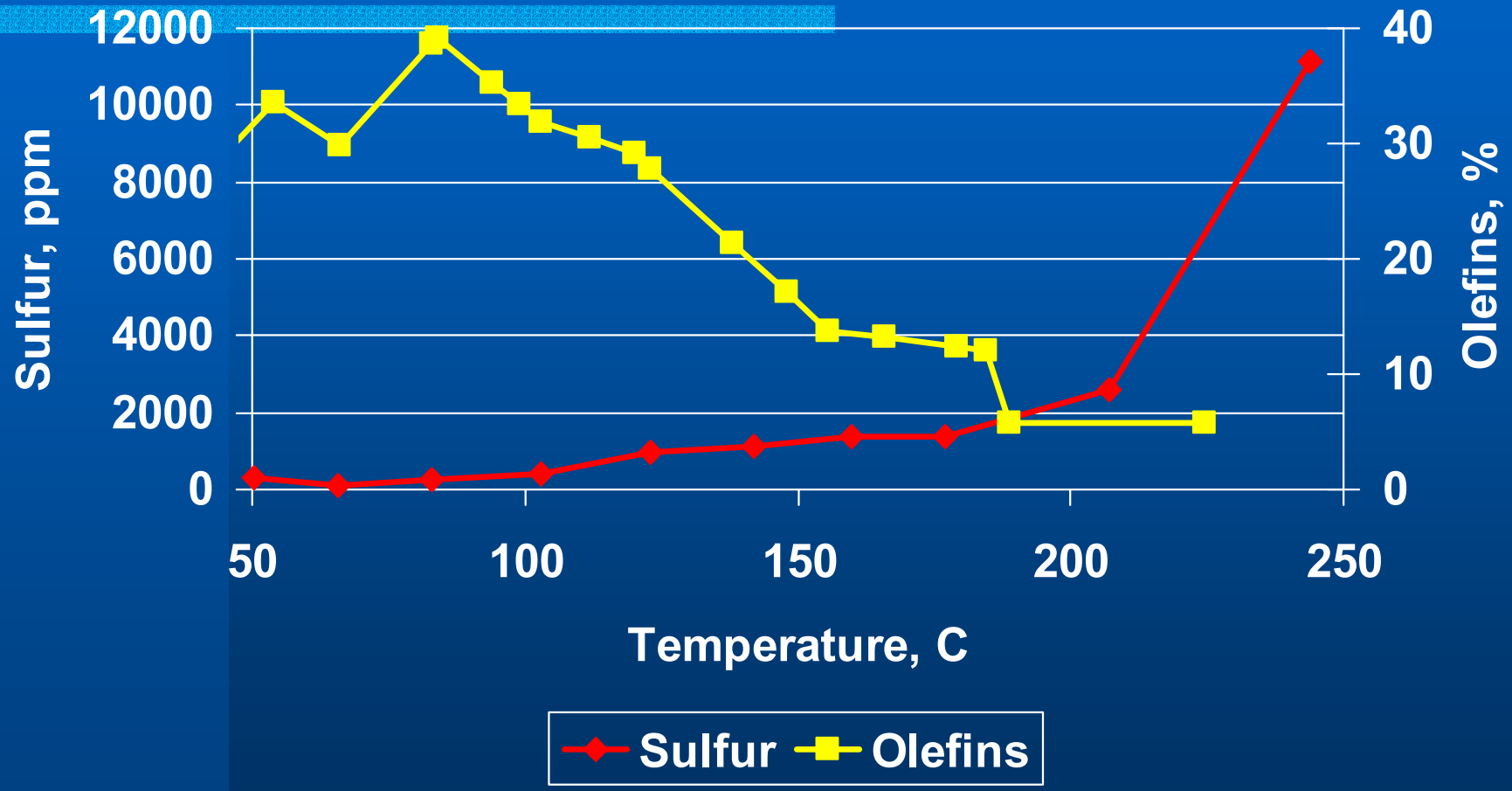
Gasoline Desulfurization Requirements

- **Pool sulfur specification**
  - **Europe**
    - **European Union**
    - **50 ppm max - 2005**
    - **10 ppm max**
    - **- available 2005**
    - **- standard 2008**
  - **US, Canada**
    - **30 ppm avg - 2002 to 2008**
  - **Future**
    - **15 -10 -5 ppm? - 2005+**

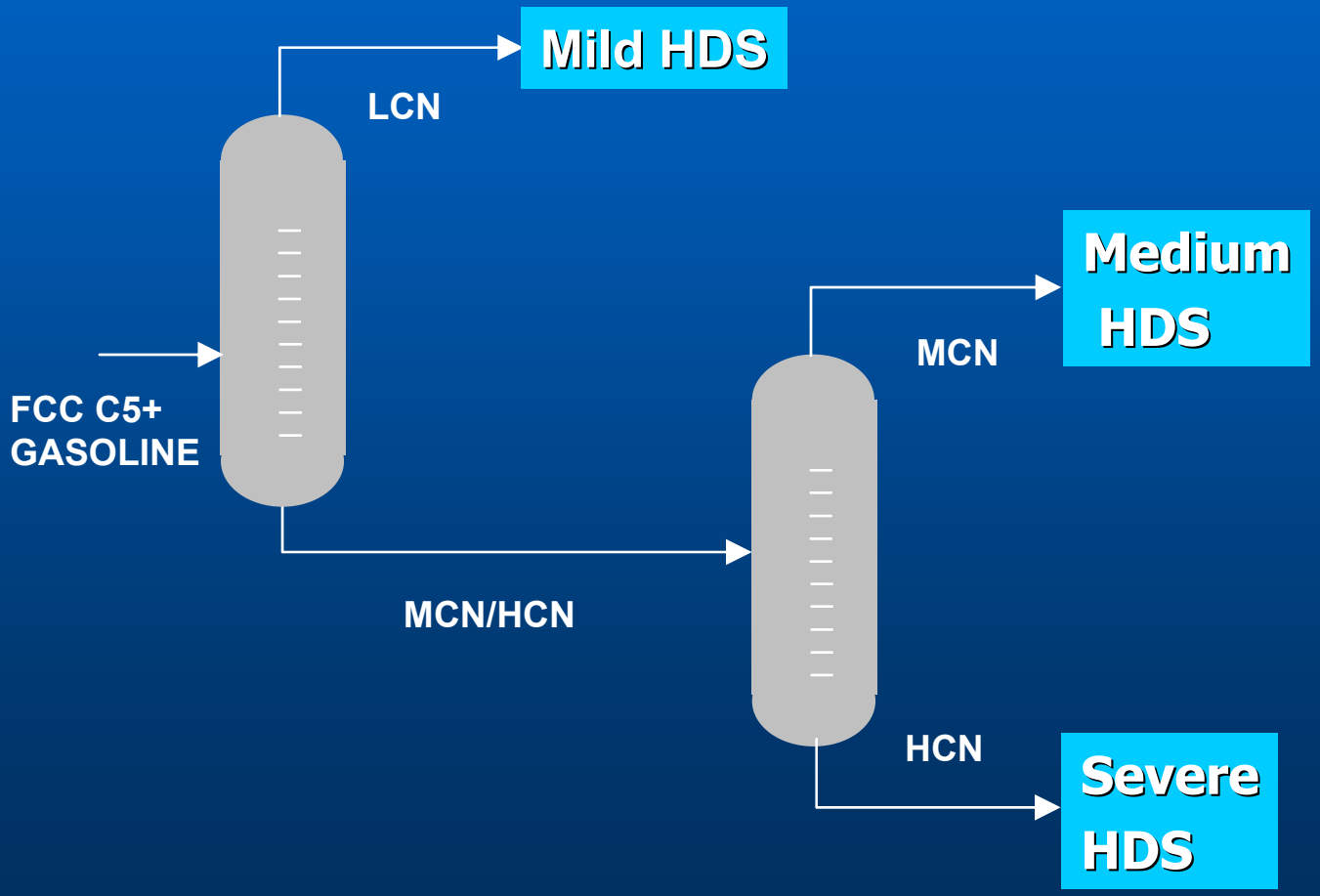
Sulfur Sources

- **FCC Naphtha**
  - **200 to 3000 ppm**
  - **25 to 40% of refinery pool volume**
  - **85 to 99% of refinery pool sulfur**

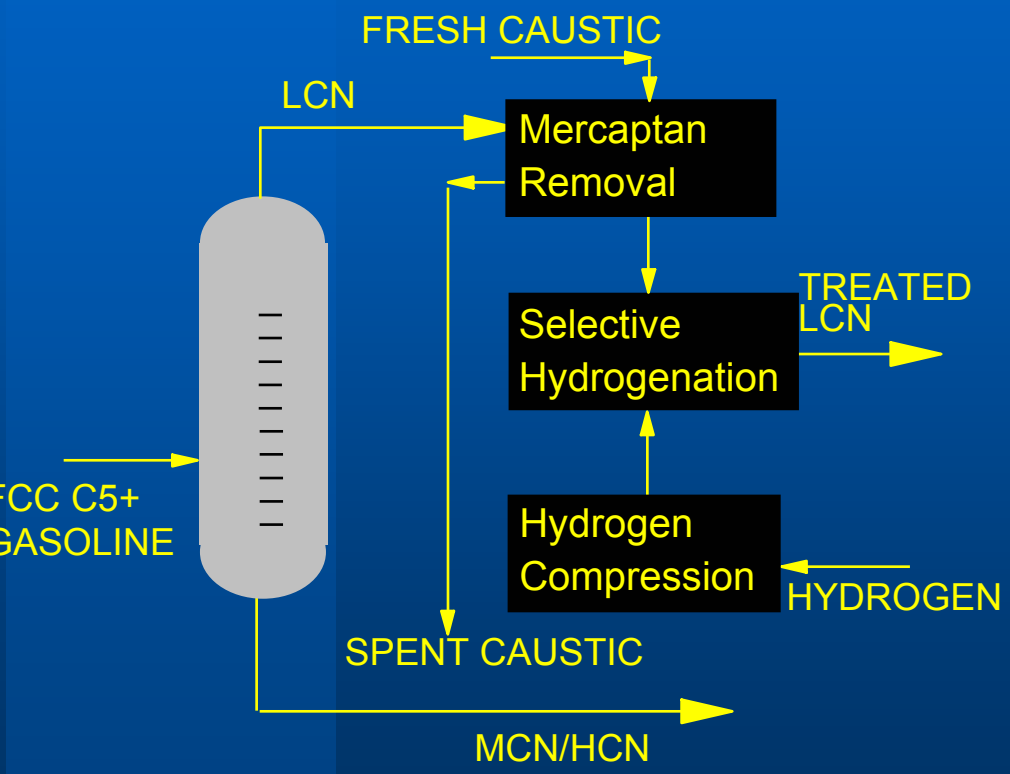
FCC Gasoline Feed Composition



Optimized HDS Process



Conventional LCN Treating

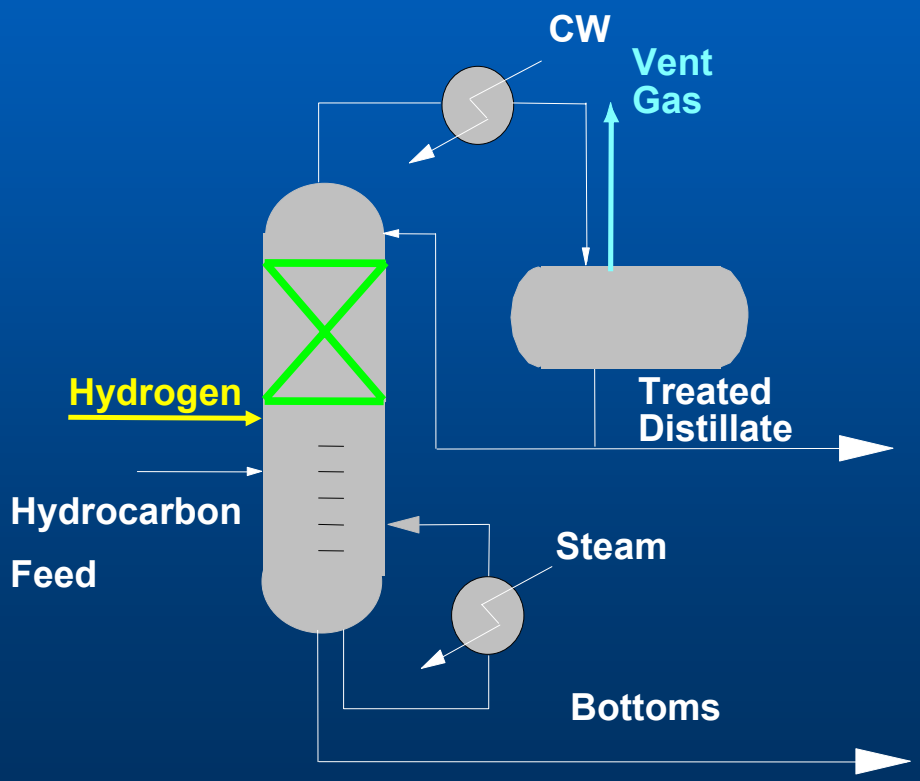


- Fractionate LCN from FCC Gasoline
- Caustic wash for mercaptan removal
  - ~90% effective
- Selective hydrogenation of dienes for alky/ethers
- Compression of makeup hydrogen

Hydrogenation / Distillation

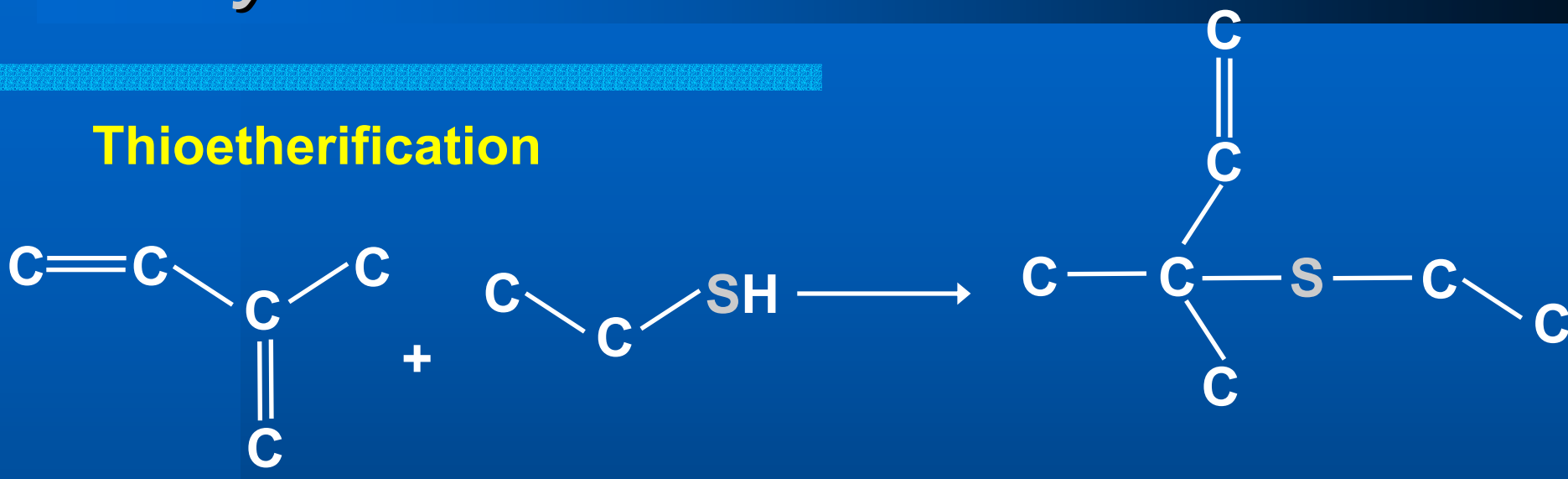
- Replace trays with structured distillation packing containing catalyst
- Add Hydrogen Feed
- Vent excess Hydrogen

CD*Hydro*® Process

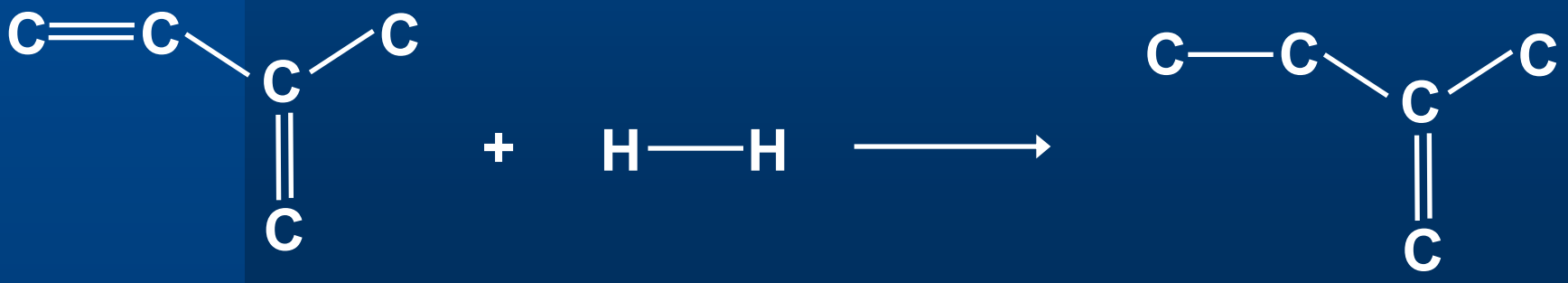


CD*Hydro* Reactions

Thioetherification

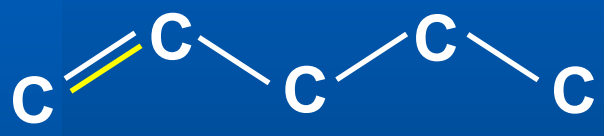


Selective Hydrogenation



CD*Hydro* Reactions

Isomerization



RON

118

CD*Hydro* Reactions

Isomerization

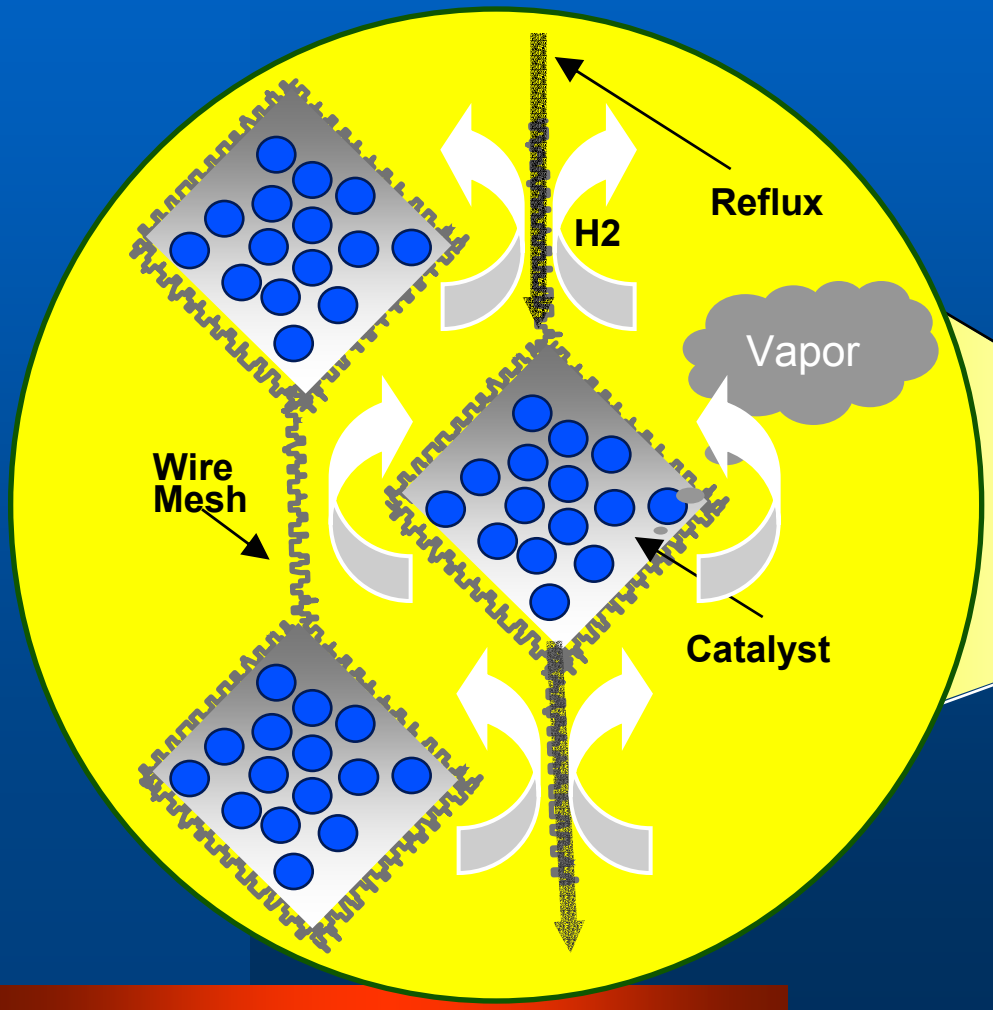
RON

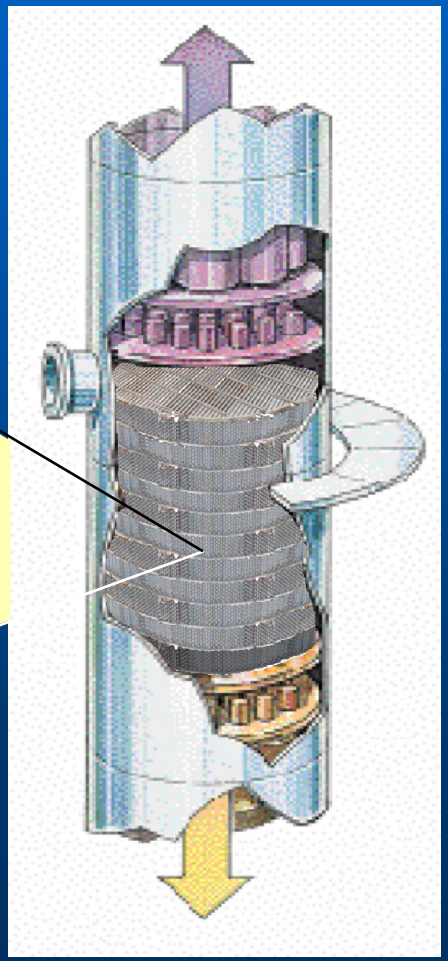
~~118~~ **150**

+0.5

Hydroisomerization boosts full range FCC naphtha by 0.5 RON

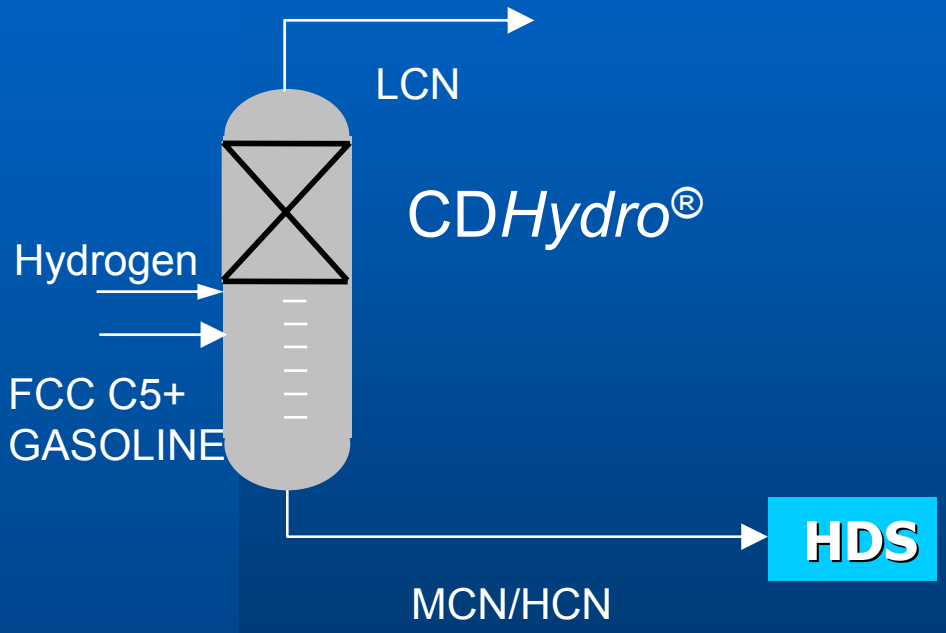
Catalytic Distillation



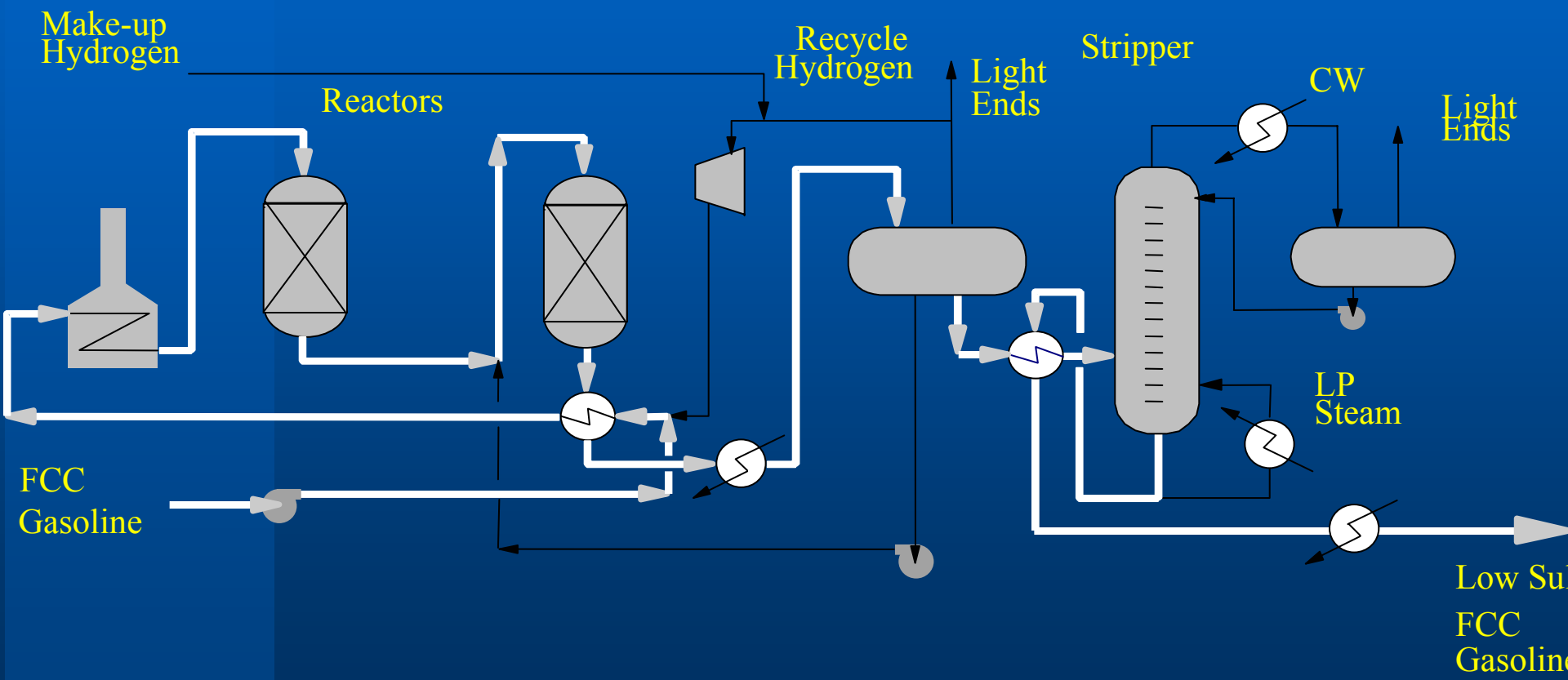


Catalyst Sectio
Drawing

Optimized FCC Naphtha HDS

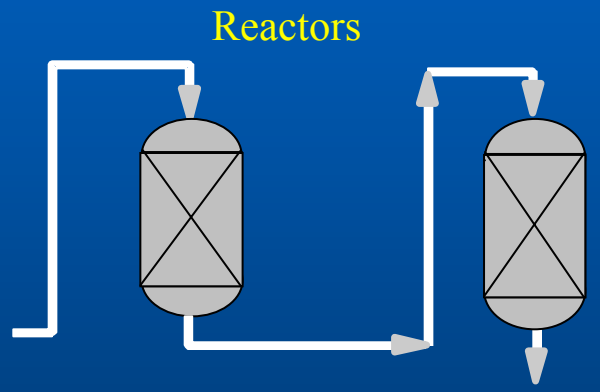


Conventional MCN/HCN HDS

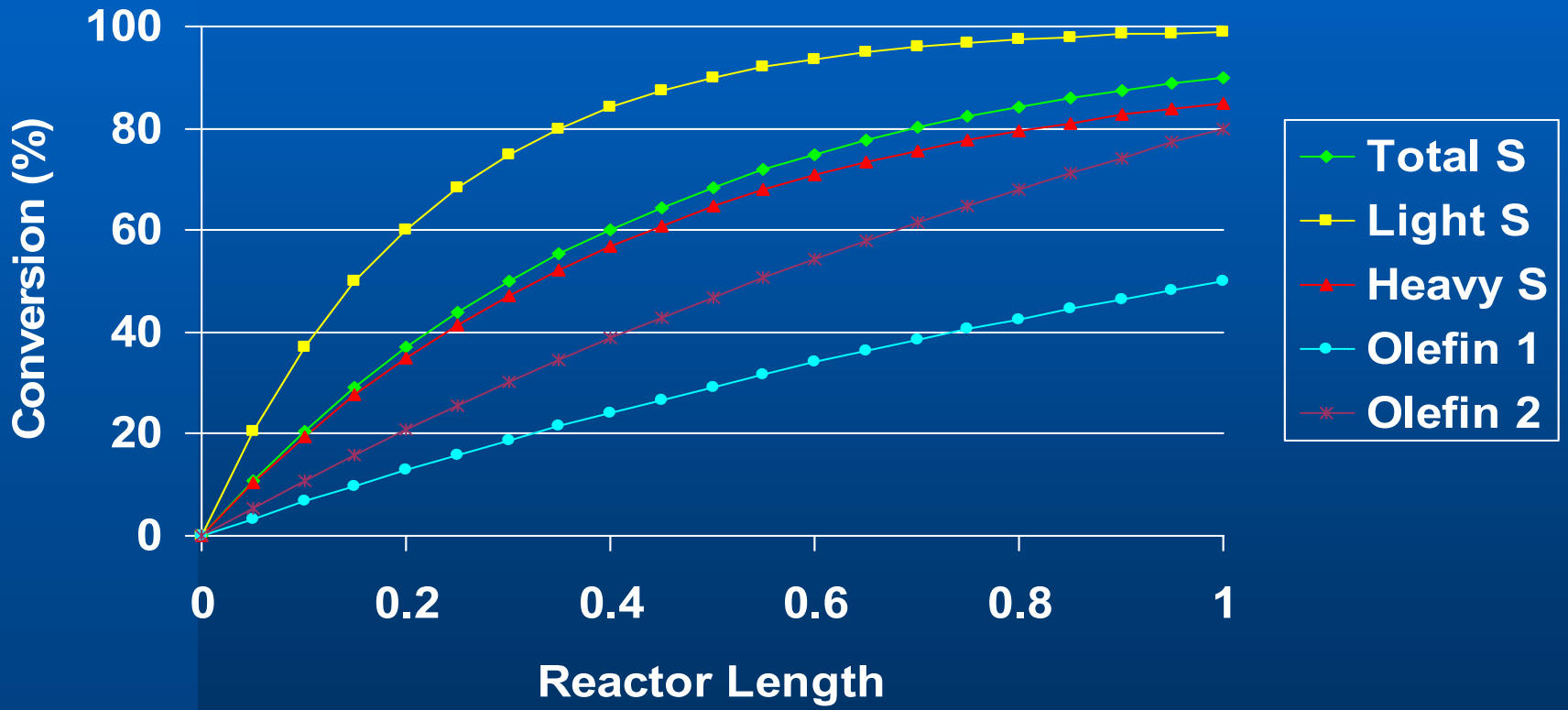


Conventional Reactor Design

- **Severity of reactor conditions set by most refractory species**
  - **Temperature**
  - **H_2 partial pressure**
- **Lighter sulfur species react to very high conversions**
- **All olefins exposed to the most severe conditions**



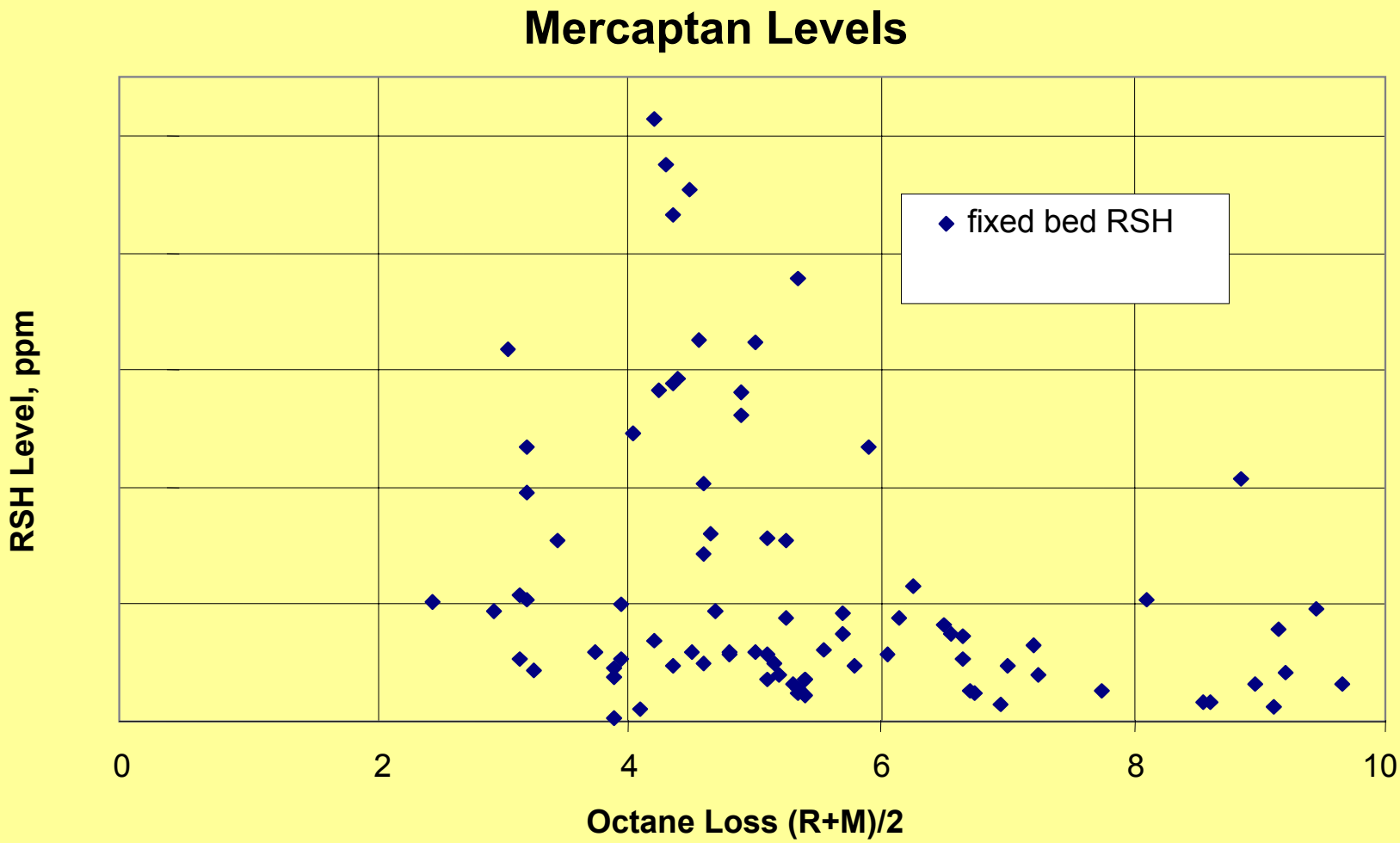
Conventional Fixed Bed HDS



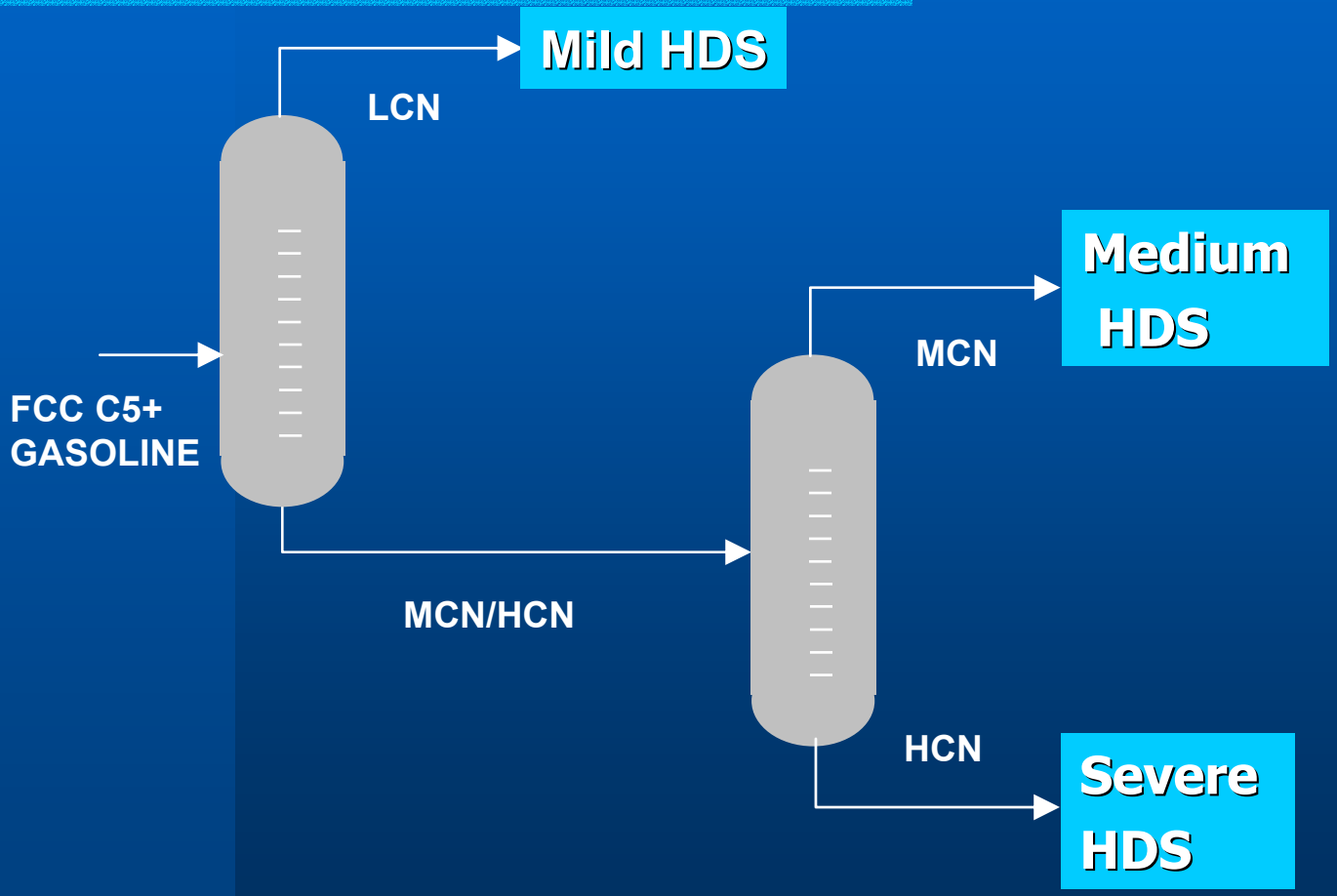
Olefin 1 - with recombinant mercaptan in product

Olefin 2 - w/o recombinant mercaptan

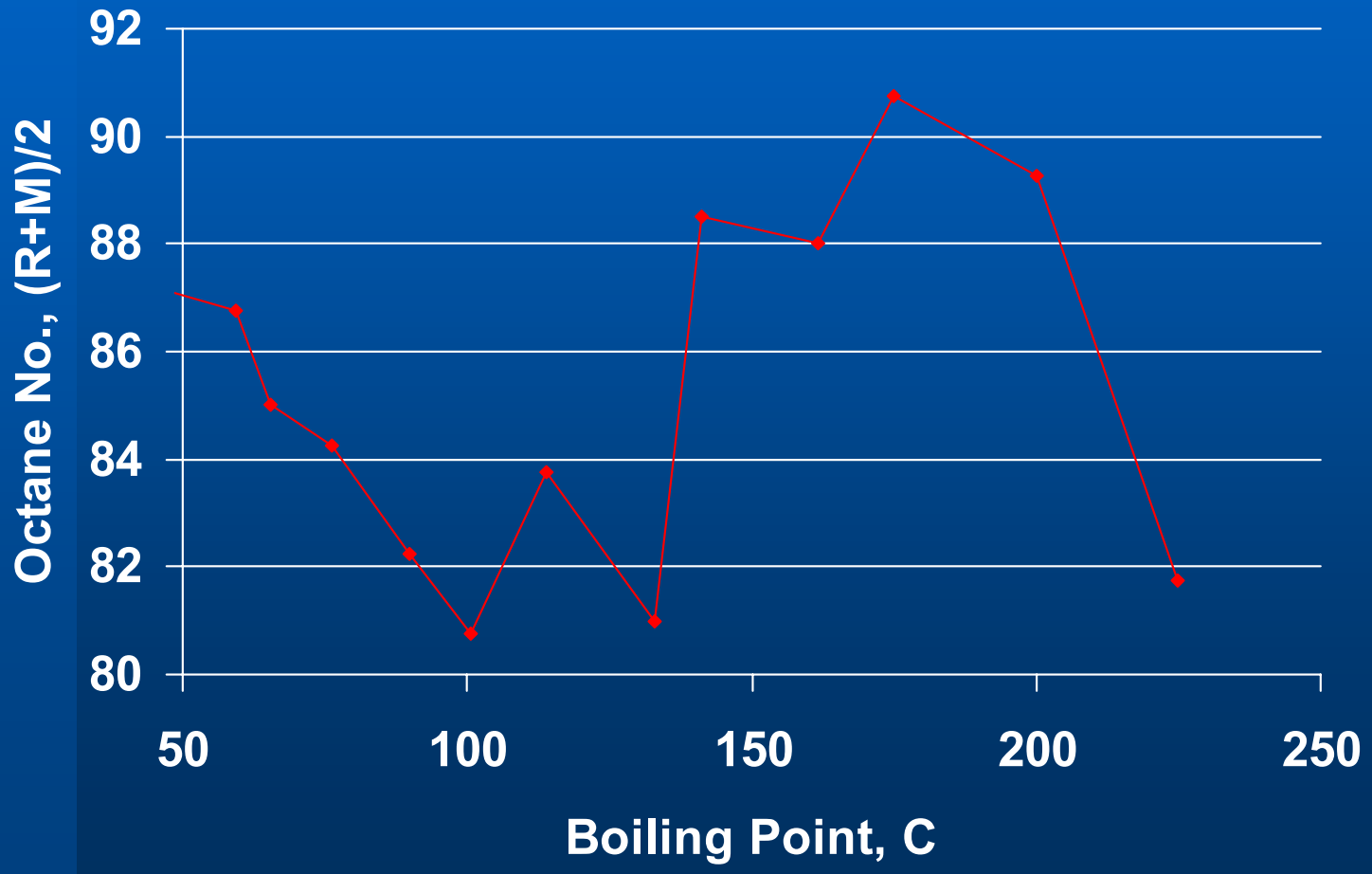
Recombinant Mercaptan Experience



Optimized FCC Gasoline HDS



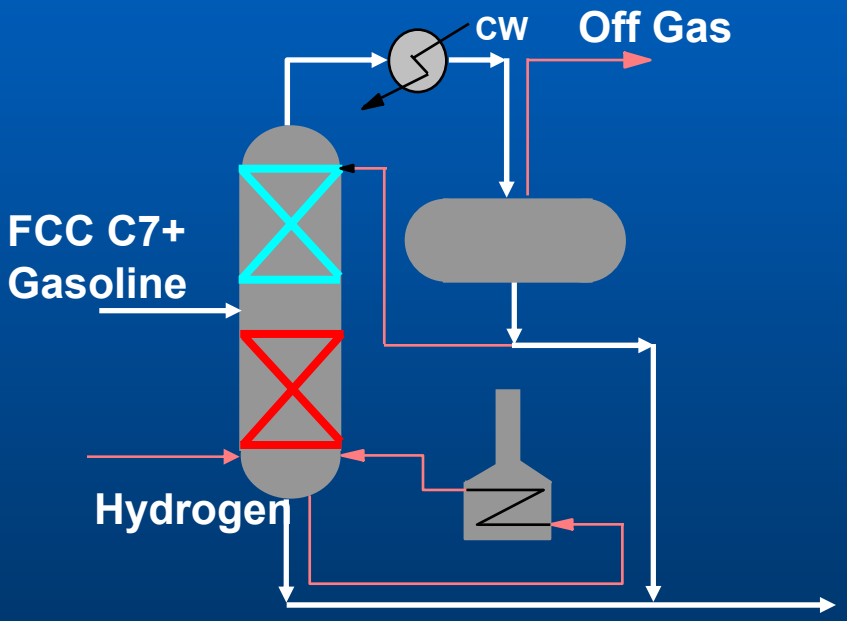
FCC Gasoline Octane Distribution



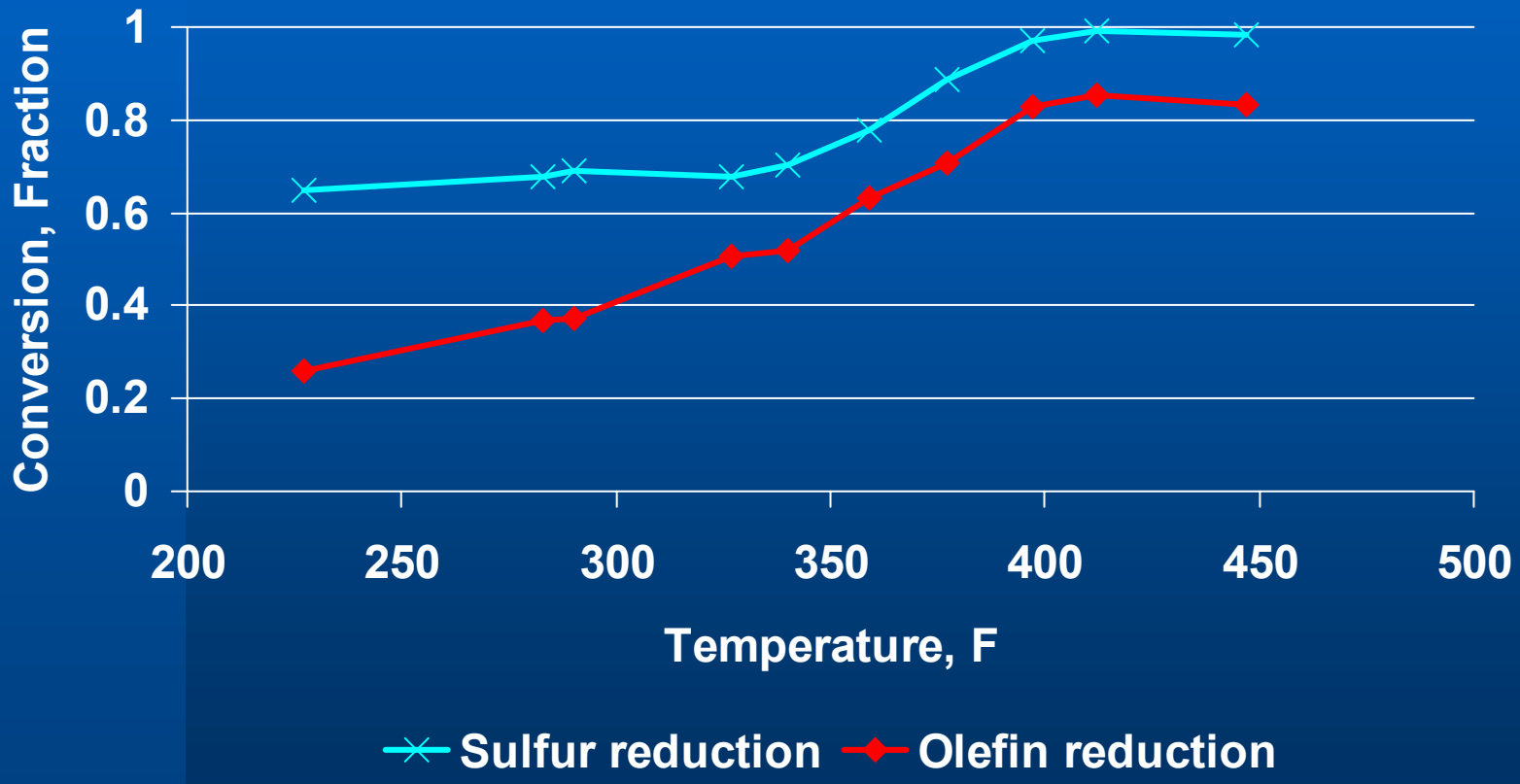
MCN/HCN with CD*HDS*

- Conditions milder than conventional fixed bed (17 barg vs 28+)
- > 99% HDS
- Heavy sulfur to bottom
- Light olefins to top
- Min octane loss(<1@ 90% HDS)
- Low H2 consumption
- Low sulfur bottoms product good for gasoline
- No yield loss due to cracking
- No makeup compressor
- No mid-cycle shutdown for catalyst regen
- No feed storage required

CD*HDS*®

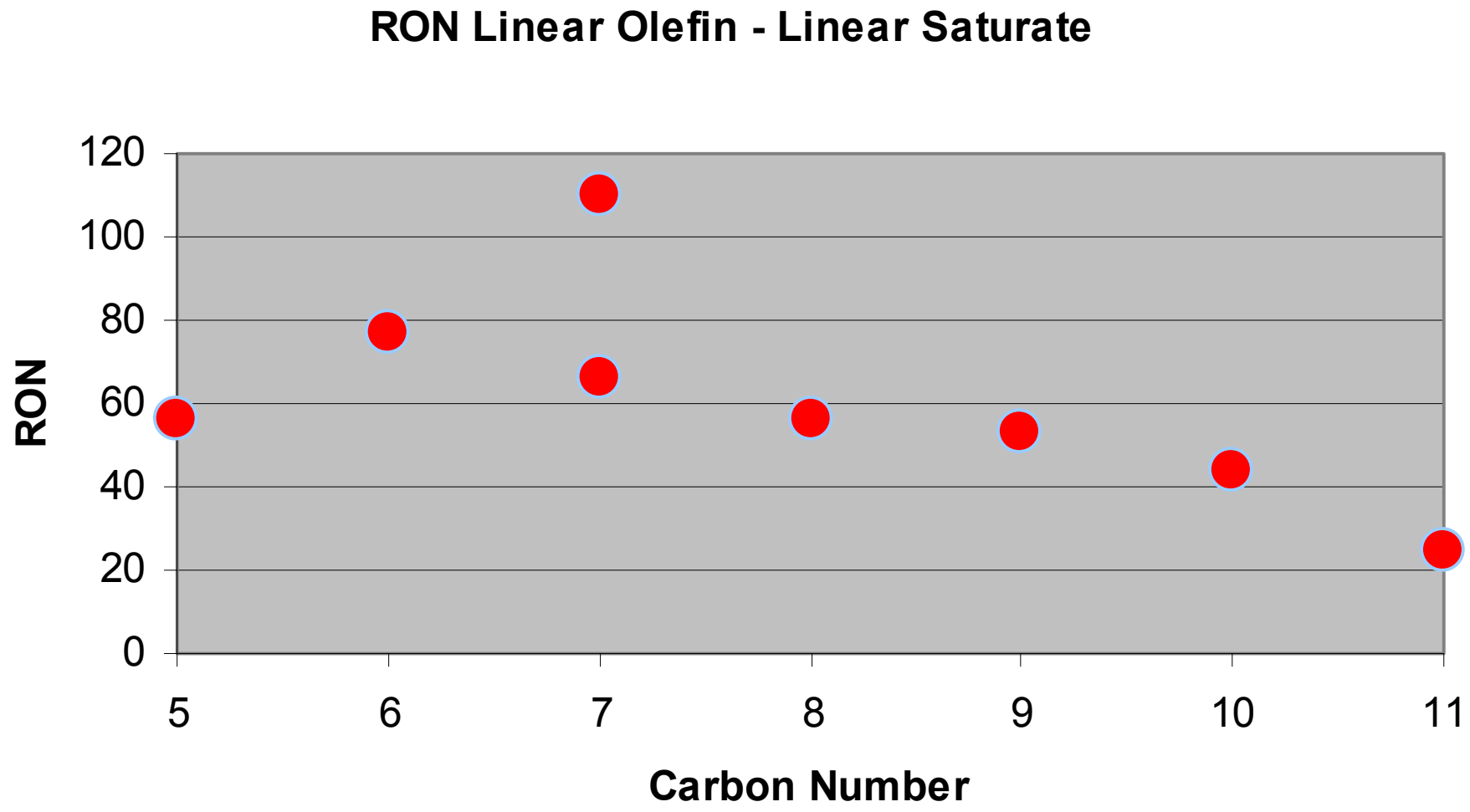


Selectivity Curve



Olefin saturation is higher for heavy olefins

Octane vs. Carbon Number



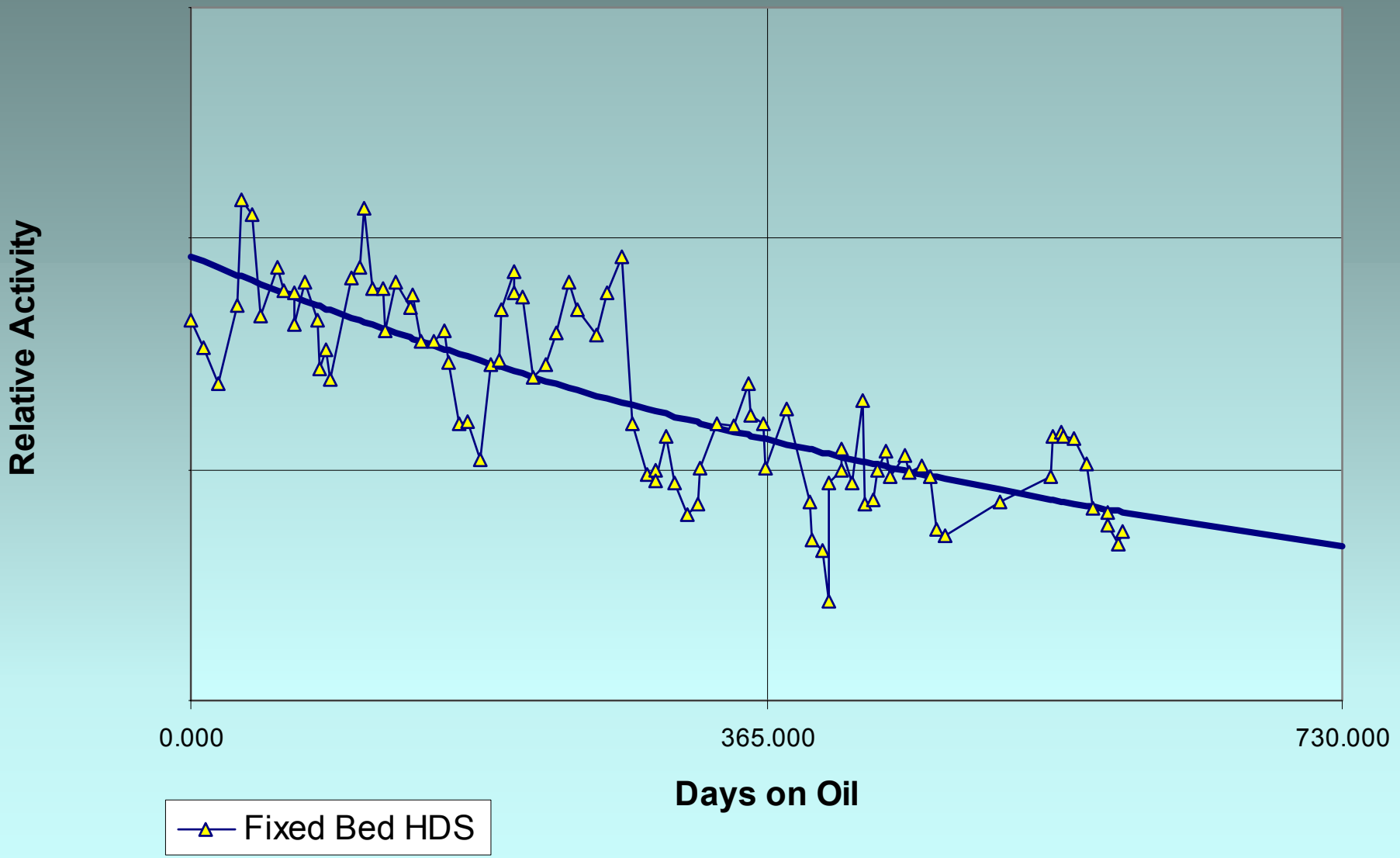
Why is CDTECH's octane loss lower?

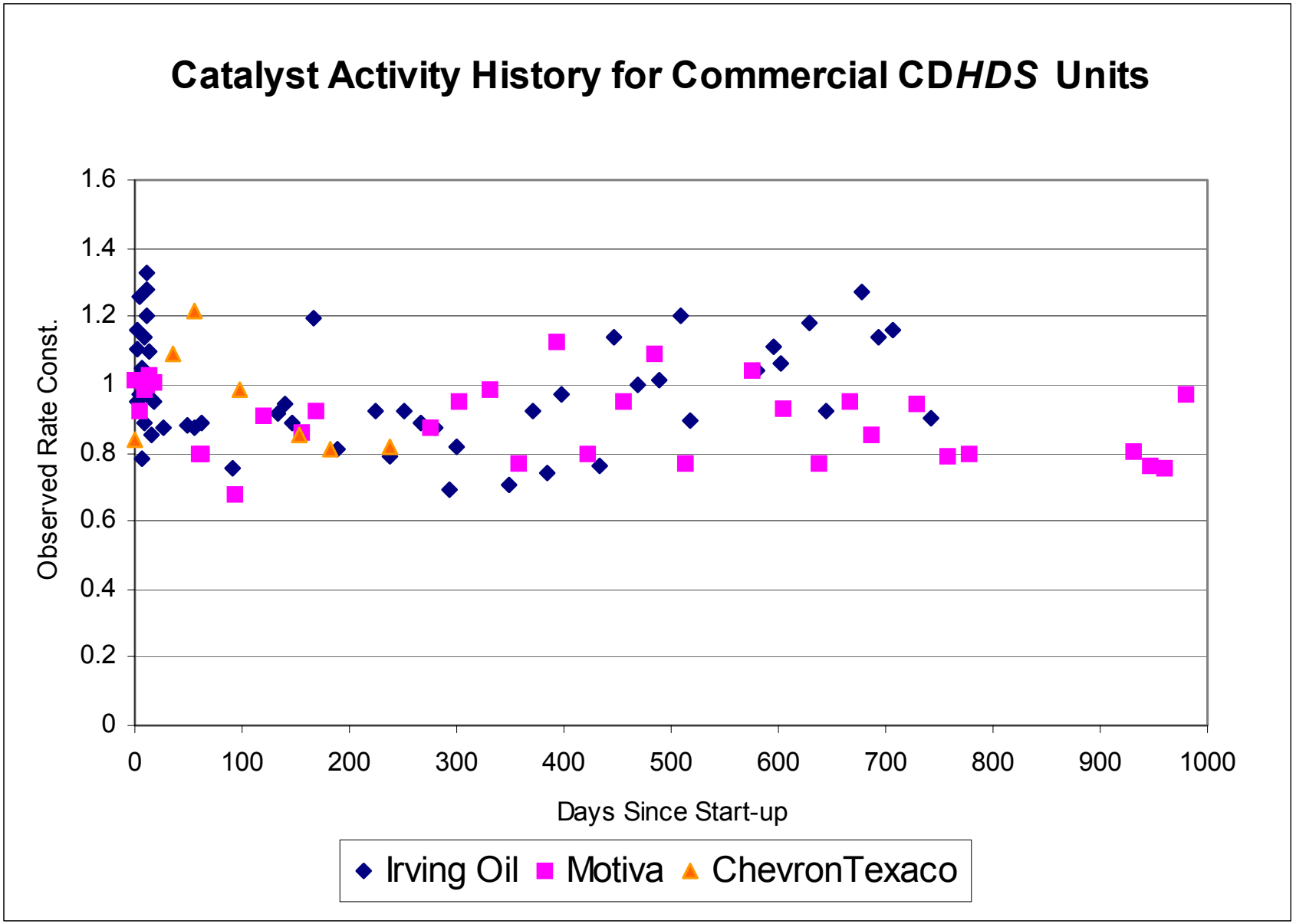
- **Conventional fixed bed hydrotreaters**
  - **Saturate primarily light olefins**
  - **Light olefin saturation causes high octane loss**
- **CD*HDS***
  - **Higher saturation of heavy olefins**
  - **Less octane to lose in heavy olefins**
  - **Lower octane loss at a given olefin reduction**

Fixed Bed HDS Catalyst Life?

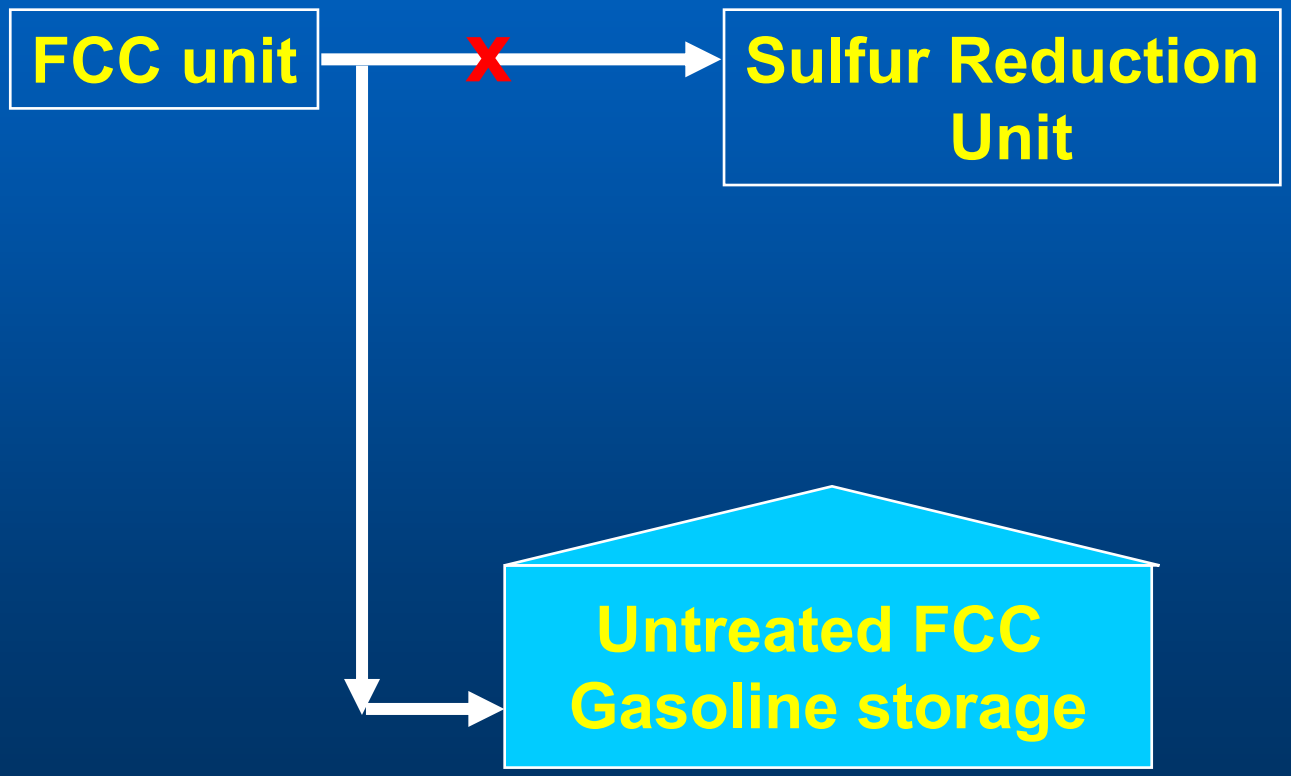
- FCC turnaround cycle
  - Modern refineries target 5 year cycle
- Conventional fixed bed hydrotreaters
  - Olefins form oligomers
  - Oligomers form coke that fouls catalyst
  - Catalyst activity reduced
  - Regenerate or replace catalyst
  - Must shutdown before end of FCC cycle
  - Fixed bed catalyst life insufficient

Commercial Catalyst Activity for FCC Gasoline HDS

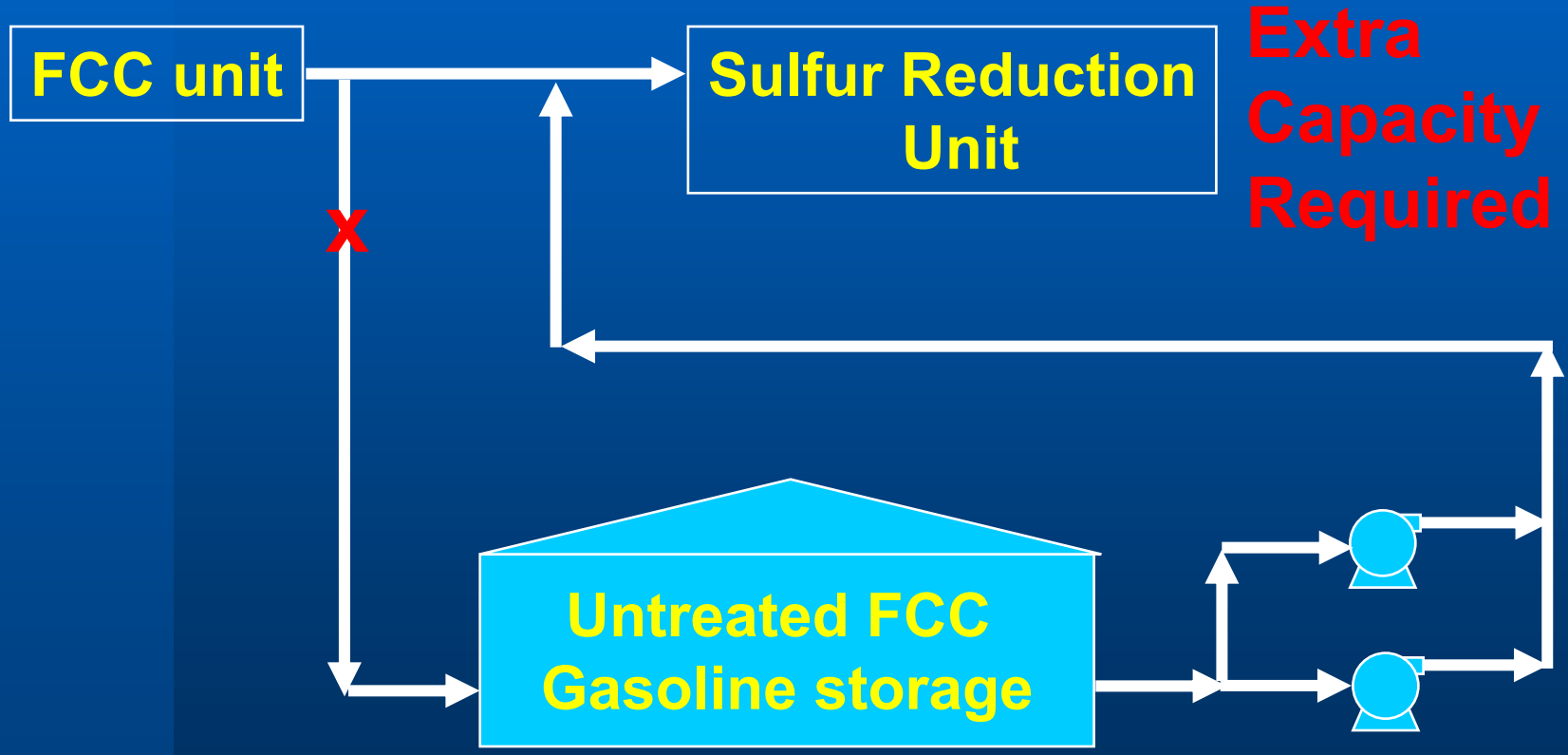



Catalyst Activity History for Commercial CDHDS Units
Observed Rate Const.
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
800
900
1000
Days Since Start-up
Irving Oil
Motiva
ChevronTexaco

Conventional Fixed Bed Unit Shutdown



Conventional Unit Restart



Conclusions

- CD*Hydro*
  - Lowest sulfur and diolefins in LCN
  - Eliminates separate mercaptan and diolefin removal units
- CD*HDS*
  - Lowest FCC cycle olefin loss via HDS
  - No cracking yield loss
  - No diene pretreatment required
  - No regeneration/feed storage required
- CD*Hydro*/CD*HDS*
  - Lowest overall octane loss
  - Commercially proven
  - Most cost effective HDS in FR FCC CN
  - Long catalyst life via catalytic distillation
  - Low capital cost

Recommendations

- Plan for 10 ppm sulfur
- Evaluate full FCC cycle performance
- Include shutdown related capital cost
- Thank you to DOE for 1980 funding for CR&L